# Section 5 NRMRL Research Results

## Primary PM From Combustion of Heavy Fuel Oils Phase I Tests

Initial experiments were conducted with the goal of understanding how PM emissions and size-specific composition changed with changes in fuel composition and operating conditions typical of small boilers commonly used in commercial, institutional, and light industrial applications. The test results indicated that modest changes in combustion conditions did not result in significant changes in PM stack concentrations or characteristics. Reducing the fuel oil feed temperature from 120 °C to 77 °C and reducing excess air to achieve 2.5% O<sub>2</sub> in the stack (compared to 3.5%) changed the total PM emission rate (lb/10<sup>6</sup> Btu or mg/kJ) by less than 5%. Similarly, changes in the loss on ignition (LOI) for particles larger than 2.5 μm in aerodynamic diameter were seen during the same tests. Increases of up to 18% in PM concentration (mg/m³) were noted during the same tests, and the LOI values for particles smaller than 2.5 μm in aerodynamic diameter also increased by roughly 20% (Miller et al. 1998).

The mass emission rates were different, but not significantly, for the four fuel oils burned (a No. 5 fuel oil and low, medium, and high sulfur No. 6 fuel oils). The differences in total mass emission rates correlated positively with unburned carbon levels (see Table 3). These results are consistent with particle composition, which showed high levels of carbon in the coarse particle fraction due to incomplete combustion in the relatively cold combustion environment of this firetube boiler design. The high carbon levels added significant mass to the total PM concentrations, resulting in the correlation between LOI and PM mass concentration.

Table 3. PM emission rates and emission factors and measures of unburned carbon for oils burned in NRMRL tests

Fuel type	Fuel Oils				Emulsified Fuels			
Combustor	Firetube Boiler			Refractory Lined Furnace			Watertube Boiler Simulator	
Fuel	No. 5	Low S No. 6	Medium S No. 6	High S No. 6	High S No. 6	No. 6	No. 2	Orimulsion 400
PM, mg/m <sup>3</sup>	197.7	219.5	243.5	183.6	93	160	3.4	160
PM, lb/10 <sup>6</sup> Btu	0.143	0.161	0.142	0.123	0.052	0.11	0.0027	0.12
PM, lb/1000 gal	21.0	24.2	21.3	18.6	7.17	15.4	0.26	12.5
Total LOI, %	NA <sup>a</sup>	NA	NA	NA	19.6	NA	NA	NA
Filter LOI, %	75.3	86.6	79.0	65.8	NA	NA	NA	NA
Cyclone LOI, %	95.5	96.9	93.6	90.3	NA	NA	NA	NA
Unburned carbon in fly ash, %	NA	NA	NA	NA	~0	NA	NA	NA

<sup>&</sup>lt;sup>a</sup> Not Available

The PSDs were consistently bimodal, with a fine mode slightly smaller than 0.1  $\mu m$  and a coarse mode near 40  $\mu m$ . This indicates two particle formation processes— vaporization followed by nucleation and condensation forming the fine particle mode and mechanical processes forming the coarse mode. This is consistent with the previously published results noted earlier. These findings are also consistent with particle images viewed under a scanning electron microscope (SEM). Many of the particles from the package boiler appeared as large (>20  $\mu m$  in diameter), porous cenospheres. These cenospheres are formed when the lighter fractions of the oil burn off, leaving the less volatile and more slowly burning char. When conditions are not hot enough or when there is not enough oxygen present, these remaining spheres composed of the heavier fractions form a char, which passes unburned out of the boiler in the form of PM. These unburned carbon cenospheres significantly increased the PM mass above what would be expected based on the fuel ash content alone (Miller et al. 1998).

The key findings from the initial phase of research are:

- Modest changes in combustion conditions, such as slightly reducing excess air and reducing the oil feed temperature, did not significantly change PM mass emissions;
- PM mass emissions from a firetube boiler do not positively correlate with oil ash content, but more closely correlate with unburned carbon levels in the ash; and
- Incomplete combustion of the carbon in the fuel results in the formation of large (> 20 μm diameter) particles that contribute substantially to the total PM mass emission rates for these boiler designs.

As this initial study was being developed, discussions with NHEERL identified an opportunity for collaboration through providing PM samples for toxicity testing. These samples were collected from the large dilution sampler shown in Figure 8, and the particles were physically removed from the filter for later toxicological tests. Although the physico-chemical properties of the samples varied only slightly, particle samples from these initial tests showed significant differences in biological response as measured by indications of pulmonary damage following intratracheal instillation of the particles into laboratory animals. These indications were most pronounced in the fine ( $<2.5~\mu m$ ) particle fraction and in the oils with the highest sulfur and transition metal contents.

#### Phase II Tests

As a consequence of these initial studies and based on understanding of particle formation mechanisms, the research turned toward examining the effects of large changes in combustion condition by comparing particles formed in two combustion systems of significantly different design. By using a hotter furnace, more complete carbon burnout would be expected to form particles that were almost entirely in the ultrafine ( $\leq 0.1 \ \mu m$ ) fraction, since the unburned carbon that formed the larger supermicron particles would be completely combusted in the hotter unit. The smaller particles were also expected to be at least as water soluble as the fine fraction generated in the initial study and would

provide NHEERL with the ability to examine the toxicological mechanisms in more detail.

Therefore, the second set of heavy fuel oil experiments was conducted on the refractory-lined Rainbow tunnel furnace. This unit generated particles that had very little unburned carbon, in contrast to the substantial amount of carbonaceous cenospheres in the firetube boiler. The dominant particle formation route in the Rainbow furnace was through vaporization and subsequent nucleation and condensation of inorganic material. This is illustrated by the single particle size mode near 0.1 µm (see Figure 9). The smaller particles generated in the Rainbow were also found to be highly water soluble, similar to

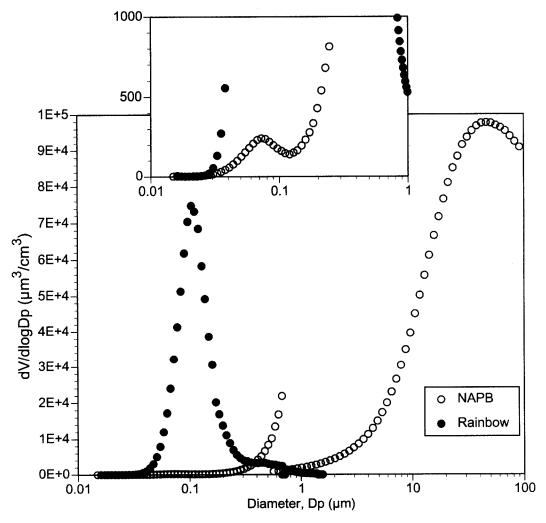


Figure 9. Particle size distributions for No. 6 fuel oil in the North American Package Boiler (open circles) and Rainbow furnace (closed circles). The inset shows details of the particle size distributions between 0.01 and 1 µm in diameter.

the fine fraction of particles from the firetube boiler. Because of the improved carbon burnout, the total PM emission rate from the Rainbow was approximately half that from the firetube boiler, even when using the same fuel at nominally similar combustion conditions (as determined by excess O<sub>2</sub>) (Linak et al. 2000b).

The emission rates from the two combustion systems were similar to values reported from commercially operating equipment, with the firetube boiler representing small commercial and industrial boilers and the Rainbow simulating larger industrial and utility boilers. Comparing the results from these first two series of tests, it is interesting to note that more complete carbon burnout resulted in significantly less total PM mass emissions, but a higher mass of the fine particles that appear to be more bioactive.

The relationship between carbon burnout (as measured by LOI) and PM mass emissions is clearly seen in Figure 10, which also shows the relationship between fuel oil ash content and PM mass emissions for the fuels and combustors used in NRMRL's experiments. The relationship between ash content and PM emissions indicates a slight inverse relationship; as ash levels in the fuel increase, PM mass emissions decrease. It is

□ Baseline, No. 5 Oil
 △ MS No. 6 Oil
 ◇ Low Oil Temp, No. 5 Oil
 ○ HS No. 6 Oil
 □ Low Stoichiometric Ratio, No. 5 Oil
 • HS No. 6 Oil, Refractory Lined Furnace
 + LS No. 6 Oil

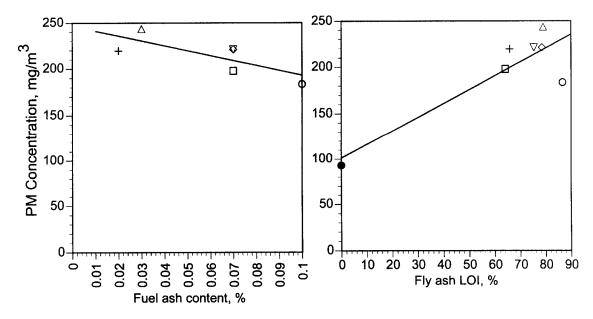


Figure 10. Stack concentrations of PM as a function of fuel ash content for the four fuel oils burned in the firetube boiler (left) and fly ash loss on ignition (right) for the four fuel oils burned in the firetube boiler and the Rainbow refractory lined furnace

unclear whether there is an underlying mechanism resulting in this relationship, but it seems unlikely that this will hold in general. For the NAPB boiler data only (i.e., ignoring the single point from the Rainbow furnace), the relationship between ash content and PM concentration shows a slightly negative correlation.

In contrast, the relationship between LOI and PM concentration is positive. Physically this makes sense because particles with high LOI contain mass that would have been converted to CO<sub>2</sub> under optimal conditions rather than remaining with the particles and contributing to the emitted mass. Although this positive correlation between LOI and PM is also evident from the samples taken from the firetube boiler, the most pronounced difference is between the Rainbow furnace and the data from the firetube boiler clustered in the upper right of Figure 10. This difference in PM mass emissions between the two systems clearly illustrates the impact of system design on emissions, with the hotter Rainbow generating approximately half the mass emissions compared to those from the firetube boiler.

The key findings from the second phase of the research are:

- Significant changes in combustion temperature and residence time due to different combustor designs result in substantial changes in PM characteristics and mass emissions;
- Combustion of heavy fuel oil under conditions simulating large industrial and utility boilers generates a nearly unimodal submicron PSD; and
- The submicron particles contain metals and sulfur that are largely in water soluble form, in contrast to the supermicron fraction of particles that contains less soluble thiophenic sulfur and metal species.

The level of unburned carbon also appears to influence the chemical species that are formed. Detailed examination of the particles from the NAPB indicate that approximately 50% of the sulfur in the particles is not oxidized, although essentially all of the sulfur in the PM collected from the Rainbow furnace is in the form of sulfates (SO<sub>4</sub>) (Huffman et al. 2000, Pattanaik et al. 2000). The form of sulfur is significant, since the sulfate form is much more soluble in water than the unoxidized organic (thiophenic) form of sulfur. Much of the sulfate in these submicron particles is combined with metals, resulting in metals with relatively high solubility in water. As noted earlier, one of the characteristics of particles from heavy fuel oil that is suspected of leading to adverse health effects is the presence of water-soluble transition metals, and metal sulfates are much more water-soluble than most other metal species that are formed in combustion systems. The combination of transition metals and high sulfate levels indicates that the Rainbow PM is likely to contain much higher levels of water-soluble transition metals than the PM from the NAPB, even though both are generated by combustion of the same fuel.

### Data from Other Studies

In addition to the conventional heavy fuel oils, two water-in-oil emulsified fuels and Orimulsion, a bitumen-in-water fuel, were also tested under other programs. PM size distributions and mass emissions were tested during these programs and provide additional information of relevance here. For the emulsified fuels tested, the presence of water in the fuel changed the way the fuels burned and resulted in noticeable changes in PM emissions and size distributions. The water in the emulsified fuel oils created "microexplosions" as the fuel is rapidly heated, thereby forming much smaller fuel droplets than could be formed by the mechanical processes of the nozzle. These smaller droplets burn more quickly, thereby reducing the amount of unburned carbon and reducing both the mass of PM emissions and the size of the emitted particles (Miller et al. 2001, Miller 1996). Even though the physical arrangement of Orimulsion is different from the water-in-oil emulsified fuel oils, the results were very similar when compared to a non-emulsified fuel oil. This is most likely due to the small size (8-20 µm diameter) of the bitumen droplets in the Orimulsion, which is much smaller than the fuel oil droplets generated by the oil nozzle (Miller and Hall 2000). The net effect of the microexplosions and subsequent smaller fuel droplets is to reduce the time needed to volatilize and combust the fuel. This reduces the impact of rapid temperature drop in systems such as the firetube boiler and results in particles with lower unburned carbon and higher fractions of submicron particles compared to non-emulsified fuels burned under similar conditions.

### Further Evolution of Research Directions

Given the successful generation, sampling, and instillation of particles in these first two series of tests, the research then moved forward along two different, but complementary, routes. The physico-chemical characterization studies of heavy fuel oil were essentially complete, but there was substantial interest in expanding the collaboration on determining toxicity by providing a source of particles for joint NMRML-NHEERL studies of direct inhalation of the particles by animals. This work has begun with initial tests using heavy fuel oil. This route of research is anticipated to continue for the foreseeable future, with the emphasis on toxicological rather than physicochemical characterization. Results from these collaborative studies are still being analyzed, but the capability to generate well characterized, real-world particles for real-time inhalation exposure studies has been demonstrated and can be applied to other source types as research needs dictate.

The second route of research stemming from the original heavy fuel oil studies was testing of pulverized coals. Although there has been much more research conducted to characterize PM generated by the combustion of pulverized coal, no physico-chemical characterization studies were known to have been conducted with the goals of quantifying the presence of water soluble transition metals and generating well-characterized primary PM samples for toxicity studies aimed at better understanding the causal mechanism of health damage associated with exposure to ambient PM<sub>2.5</sub>.

### **Primary PM From Combustion of Coals**

Nine different U.S. coals were burned during NRMRL's PM characterization tests. These coals were chosen to represent different regions of the U.S. and have different sulfur and trace element contents (see Table 1) as well as different ash chemistry. The initial tests focused on particle size, mass, and composition measurements for the coals burned in the down-fired IFR.

PM concentrations generated by the combustion of coal were much higher than for the fuel oils, as shown in Table 4. This is expected because of the significantly higher amount of inorganic ash present in the coal (8-20%) compared to the fuel oils (usually much less than 1%). Uncontrolled mass concentrations for the coals tested were over 20 times higher than those for the heavy fuel oil, which is similar to the ratio of inorganic ash contents of the coals versus the fuel oils. However, most of the coal PM mass is in the larger (>5 µm diameter) size fractions, with only about 4 to 7% of the total PM mass associated with PM2.5. The unburned carbon values measured in EPA's experiments were slightly higher than, but not atypical of, many utility-scale boilers and considerably less than the LOI values for the PM from heavy fuel oil burned in the NAPB (Linak et al. 2000a). However, because of the much higher levels of inorganic material in coal compared to that in heavy fuel oil, it can be misleading to directly compare fractions of unburned carbon or LOI for the two fuel types. For instance, 5% unburned carbon for a coal-generated PM may translate into more total mass of unburned carbon than 80% unburned carbon for PM from the combustion of heavy fuel oil. The much higher inorganic content in coal also results in unburned carbon having a much lower effect on PM mass emissions for coal than for oil, since coal PM mass emission rates are dominated by the inorganic material present in the fuel.

**Table 4.** PM emission rates and emission factors and measures of unburned carbon for coals burned in NRMRL tests.

Fuel Type	Bituminous Coals				Subituminous Coal		Lignite
Fuel	Ohio 5,6,7 Blend	Pitts- burgh 8	Utah	West Ken- tucky	Montana	Wyodak (PRB <sup>(a)</sup> )	North Dakota
PM, mg/m <sup>3</sup>	4477	3565	4323	3807	4374	3441	5582
PM, lb/10 <sup>6</sup> Btu	3.70	2.71	3.32	3.00	3.30	2.63	6.02
PM, lb/ton	95.2	70.3	74.9	67.9	62.8	46.6	77.0
Unburned carbon in fly ash, %	NAª	NA	10.9	10.2	0.5	NA	NA

<sup>&</sup>lt;sup>a</sup> Not available

NRMRL's experimental results demonstrate some of the different mechanisms involved in particle formation during coal combustion. Figure 11 presents typical particle size distributions for several of the coals tested. The three distinct modes indicate different formation mechanisms. The smallest mode occurs near 0.1  $\mu$ m in diameter and is due to the vaporization and subsequent nucleation and accumulation similar to that in the

ultrafine particles from heavy fuel oil combustion. These particles tend to be enriched in metals that have volatilized and nucleated and to have high levels of sulfates. The second mode occurs between 0.8 and 2.0  $\mu$ m in diameter and has not been commonly identified in previous studies. This mode is believed to be composed of fragments of ash particles originally contained within the pulverized coal particles. The third mode begins near 10  $\mu$ m diameter and is formed largely by coalescing inorganic material that is produced as the carbonaceous coal char burns away. The two largest modes have similar composition, indicating similar mechanical mechanisms of formation (Linak et al. 2001, Shoji et al. 2000). The similarity in composition supports the hypothesis that the 0.8-2  $\mu$ m particles were originally part of the larger (>10  $\mu$ m) particles, which fragmented to form the

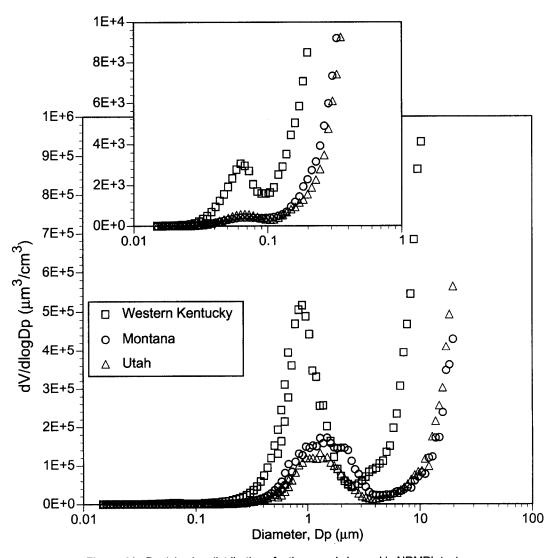


Figure 11. Particle size distributions for three coals burned in NRMRL tests.

 $0.8-2~\mu m$  particles. Both these larger modes significantly differ in composition from the submicron mode.

As is the case for PM from heavy fuel oils, the particles larger than 1 µm are formed by primarily mechanical means and will contain metals in forms that are tightly bound physically and chemically. This will result in water solubility that is significantly lower than that seen for PM from heavy fuel oils. The submicron particles, formed via vaporization, nucleation, and condensation, will be composed in part of metal and other sulfates that have a much higher solubility in water, and are therefore expected to have a higher level of bioavailability.

Figure 12 illustrates the relationships between coal ash content and PM mass concentrations, and LOI and PM mass concentrations. Note the contrast between these relationships and those for the heavy fuel oils (see Figure 10). For coal, the fuel ash content has a significant effect on PM concentrations, while LOI has minimal, if any, effect. As noted above, this is due to the much higher ash content in coals that overwhelms any significant effect from LOI.

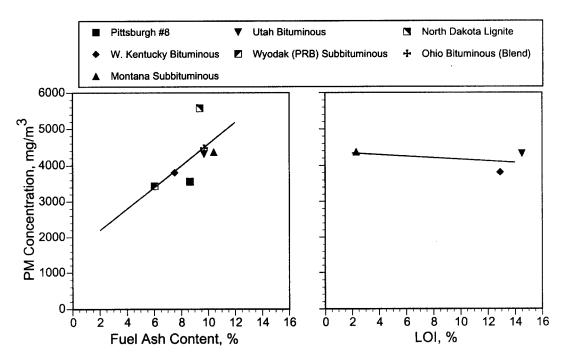


Figure 12. Stack concentrations of PM as a function of fuel ash content (left) and fly ash loss on ignition (right) for the seven coal burned in the innovative furnace reactor.

The presence of the "fine fragmentation" mode between 0.8 and 2.0  $\mu$ m means that the PM<sub>2.5</sub> from coal combustion will be composed of particles formed by different mechanisms, and with different chemical compositions. The fine fragmentation mode

makes up the majority of coal-generated  $PM_{2.5}$  mass and has characteristics similar to the coarse (>2.5 µm) particle fraction. These particles will contain significant amounts of silica and alumina compounds that tie up many of the other trace elements, including the transition metals. On a per-unit-mass basis, therefore,  $PM_{2.5}$  from coal combustion is likely to contain less water-soluble transition metals compared to  $PM_{2.5}$  from heavy fuel oil. Even so, there will remain in coal-generated PM an ultrafine fraction that is expected to be more similar in composition and physical characteristics, and possibly in toxicological characteristics, to the ultrafine fraction in  $PM_{2.5}$  from heavy fuel oil combustion.

As was the case for PM from heavy fuel oil, these results emphasize that particle size and composition are a consequence of the formation processes. The larger particles (>0.8  $\mu$ m) are formed by processes that do not involve vaporization and are therefore less likely to undergo significant chemical change. On the other hand, the ultrafine particles that do vaporize are more likely to undergo the same types of chemical reactions that favor the formation of water soluble metal sulfates.

The hypothesis that the submicron fraction of the coal generated PM may be more bioactive than the larger particle fractions has led NRMRL researchers to begin efforts to collect larger quantities of these particles. Because they make up such a low percentage of the total particle mass, however, such collection requires different particle generation and collection techniques. One approach is to begin with micronized coal, which is ground to a much finer size ( $\sim 5~\mu m$ ) than standard pulverized coal ( $\sim 70~\mu m$ ). This approach is expected to generate a substantially higher fraction of the ultrafine particles of interest, making collection of significant quantities of these particles for NHEERL toxicity studies much more efficient. Initial efforts in this area are promising and are ongoing at the writing of this report.

The key findings from this segment of the NRMRL research program are:

- A previously unreported particle mode between 0.8 and 2.0 μm contributes to the mass of PM<sub>2.5</sub> from the combustion of pulverized coal;
- The composition of particles in this "fine fragmentation" mode is similar to that of the
  coarse mode particles, suggesting that the mode is formed by coarse ash particles that
  fragment during the combustion process. The composition also suggests that these
  particles will have metals with relatively low water solubility and therefore relatively
  low bioavailability; and
- The ultrafine fraction of coal-generated particles has composition similar to that of the ultrafine mode of particles from heavy fuel oil combustion, suggesting that the pulmonary toxicity of ultrafine particles from coal combustion may be similar to the heavy fuel oil ultrafine particles.

### **Model Predictions**

In addition to the experimental program, NRMRL researchers also used computer models to help explain the behavior and speciation of particles. These models were used to simulate the major chemical and physical processes governing the formation and speciation of particles and to provide data to which the experimental results could be compared. This approach provided guidance in interpreting the experimental results and was especially useful in gaining a better understanding of the metal species likely to be present in the ultrafine PM.

### Chemical Equilibrium Modeling

Chemical equilibrium calculations allow one to identify chemical species that will form with adequate time at a given temperature. While they do not account for the effects of incomplete mixing or chemical reactions that do not have adequate time to go to completion (kinetics), equilibrium results can be used to determine what chemical species are likely to be present in a given environment and how changes in temperature or presence of other compounds can influence the speciation in the flue gases.

Thermochemical predictions for a simulated heavy fuel oil were determined using the Chemical Equilibrium Analysis (CEA) computer code for calculating complex chemical equilibrium compositions (McBride et al. 1993) with thermochemical data taken from the literature (see Linak et al. 1999, 2000b). Of interest is the predicted partitioning between vapor and condensed phases as well as elemental speciation. Using experimental data from NRMRL tests (Miller et al. 1998), CEA predicted that seven inorganic elements of potential interest to toxicologists were likely to form vapor phase species in the high temperature regions of combustion systems. All seven of these elements were also predicted to form sulfates at temperatures typical of exhaust stacks (Linak et al. 1999, 2000b). These results were consistent with the study of Huffman et al. (2000) that analyzed for several species in the fine and coarse fractions of oil-generated PM samples collected during the NRMRL experiments. Taken together, the computational and analytical results demonstrate that the formation of water soluble sulfate species is favored by the conditions present in large industrial and utility boilers.

# Aerosol Nucleation and Coagulation Modeling

In addition to modeling the chemical processes, NRMRL researchers also used a multi-component aerosol simulation (MAEROS) code (Gelbard and Seinfeld 1980) to model the physical evolution of particle sizes. The purpose of these calculations was to determine whether the experimental data were consistent with the calculated predictions to support the interpretation of the experimental results. A secondary objective was to examine the effects of particle coagulation on particle size distributions, specifically to evaluate how changes in the vaporized inorganic material would impact PSDs.

Beginning with initial conditions based on NRMRL experimental results, MAEROS predicted PSDs similar to those measured during the heavy fuel oil tests. The

consistency of the model and experimental results indicated that NRMRL's interpretation of the particle formation mechanisms based on the experimental data is reasonable (Linak et al. 1999, 2000b).

# Section 6 Summary and Implications

### **Summary**

In summary, NRMRL's combustion PM research has found the following:

- Increased unburned carbon results in increased PM mass emissions and increased particle size when burning heavy fuel oil.
- Use of emulsified fuel oils reduces both the PM mass and the particle size compared to a non-emulsified fuel oil.
- Unburned carbon does not affect PM mass emissions or particle size distributions nearly as strongly for coal as for heavy fuel oil.
- For all fossil fuels tested, the submicron particles tend to have higher concentrations of metals and sulfates than particles larger than 1  $\mu$ m in diameter.
- The water solubility of metals is significantly higher for the total PM from heavy fuel oils than for the total PM from pulverized coal, although the similar compositions of the ultrafine fractions of both fuels suggests the difference for this fraction is much smaller.
- A fine fragmentation mode between 0.8 and 2.0 μm exists in PM generated from the combustion of pulverized coal. The particles in this mode are of similar composition to the particles in the coarse (>2.5 μm) mode.

### **Implications**

Particle composition varies considerably with size, with potentially significant implications for particle toxicity. NRMRL's research, consistent with previous work, has identified significant variation in particle composition as a function of particle size. The submicron particle fractions were consistently composed of metal and other sulfates that are highly water soluble, meaning that they are more likely to interact with biological tissues when inhaled. The formation mechanisms that generate these particles govern both size and composition. Therefore, the question of whether size or composition plays a dominant role in causing adverse health effects may be inappropriate, since the two (size and composition) cannot be separated in real-world systems. It may be more relevant to focus on particles with similar formation processes rather than on particles with specific characteristics that cannot be naturally separated. In short, multiple mechanisms are involved in the formation of PM<sub>2.5</sub> from combustion sources, and these mechanisms will directly impact the role of particles in causing adverse health effects.

The design and operation of a source can result in significant changes in the physico-chemical and toxicological characteristics of the particles generated. This finding has scientific and potentially regulatory implications. In the context of toxicological research, more emphasis needs to be placed on how particle samples are generated and collected. PM toxicological studies often do not adequately describe the source characteristics, including system design, the conditions at which the system is running, or the methods used to extract particle samples. PM from heavy fuel oil, as

demonstrated here, is not a homogeneous material with consistent characteristics. In order to develop an adequate understanding of the health effects associated with PM and the causal mechanisms leading to those effects, studies must provide enough information to allow the reader to understand the representativeness of the particles used in the tests.

From a regulatory perspective, these results may eventually be used to identify source types that have the potential for emitting particles having characteristics closely associated with health risk. As additional understanding is gained regarding links between health effects and particle characteristics, it may someday be possible to develop regulatory approaches to reduce PM emissions from a more limited range of source types or to minimize emissions of particles with certain characteristics. If enough information on adverse health effects due to water-soluble ultrafine particles is developed, for instance, limits on emissions of these particles may replace or supplement limits on total mass emissions.

# Section 7 Future Directions

NRMRL's research to characterize primary particles from the combustion of pulverized coal and heavy fuel oils has been completed. There remain numerous research opportunities in the broader area of combustion-generated particles, which will be followed as appropriate. Immediate efforts will focus on characterizing emissions from small off-road diesel engines, which will involve more organic analysis, as compared to the significant levels of inorganic analysis conducted for the previous studies. Several efforts associated with the collaborative studies linking the physicochemical properties of combustion-generated particles to measures of toxicity during direct inhalation exposures will continue. This area of work shows considerable promise for generating data that can be used to better understand the links between sources and adverse health effects.

The capabilities developed during the work described in this report will continue to generate state of the art research. NRMRL's flexible and unique facilities, in combination with ORD's on-site expertise, provide unique opportunities for leading edge multidisciplinary research in PM, air toxics, and other air programs.

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# Section 8 Publications from NRMRL's Combustion-Generated PM Research Program

The 10 articles listed below represent key publications generated from the work described above (NRMRL authors noted in boldface). In addition to these publications, an additional 12 papers were prepared and presented at technical conferences between 1997 and 2002.

Huffman, G.P., Huggins, F.E., Shah, N., Huggins, R., Linak, W.P., Miller, C.A., Pugmire, R.J., Meuzelaar, H.L.C., Seehra, M.S., and Manivannan, A. (2000). "Characterization of fine particulate matter produced by combustion of residual fuel oil," *Journal of the Air & Waste Management Association*, Vol. 50, 1106-1114.

Linak, W.P., Miller, C.A., Wendt, J.O.L., and Dreher, K. (1998). "Fine particulate from residual fuel oil combustion: Physical, chemical, and health effect characteristics," 17th Annual Conference of the American Association for Aerosol Research, June 22-26, 1998, Cincinnati, OH.

Linak, W.P., Miller, C.A., and Wendt, J.O.L. (1999). "Fine particle emissions from residual fuel oil combustion: characterization and mechanisms of formation," 5th International Conference on Technologies and Combustion for a Clean Environment, July 12-15, 1999, Lisbon, Portugal.

Linak, W.P., Miller, C.A., and Wendt, J.O.L. (2000). "Comparison of particle size distributions and elemental partitioning from the combustion of pulverized coal and residual fuel oil," *Journal of the Air & Waste Management Association*, Vol. 50, 1532-1544.

Linak, W.P., Miller, C.A., and Wendt, J.O.L. (2000). "Fine particle emissions from residual fuel oil combustion: characterization and mechanisms of formation," *Proceedings of the Combustion Institute*, Vol. 28, 2651-2658.

Linak, W.P., Miller, C.A., Seames, W.S., Wendt, J.O.L., Ishinomori, T., Endo, Y., and Miyamae, S. (2002). "On trimodal particle size distributions in fly ash from pulverized coal combustion," *Proceedings of the Combustion Institute*, Vol. 29, in press.

Miller, C.A., Linak, W.P., King, C., and Wendt, J.O.L. (1998). "Fine particle emissions from heavy fuel oil combustion in a firetube package boiler," *Combustion Science and Technology*, Vol. 134, 477-502.

Pattanaik, S., Huggins, F.E., Huffman, G.P., **Linak, W.P., and Miller, C.A.** (2000). "XAFS spectroscopy analysis of the molecular structure of metals and sulfur in fine particulate matter (PM) derived from the combustion of residual oil," *ACS Fuel Chemistry Division*, Vol. 46.

Shoji, T., Huggins, F.E., Huffman, G.P., **Linak, W.P., and Miller, C.A.** (2000). "XAFS spectroscopy analysis of the molecular structure of metals in fine particulate matter (PM) derived from the combustion of coal," *ACS Fuel Chemistry Division*, Vol. 46.

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#### 15. SUPPLEMENTARY NOTES

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#### 16. ABSTRACT

Researchers at the U.S. Environmental Protection Agency's Office of Research and Development (ORD) have conducted a series of tests to characterize the size and composition of primary particulate matter (PM) generated from the combustion of heavy fuel oil and pulverized coal. These tests, conducted at ORD's National Risk Management Research Laboratory (NRMRL) in Research Triangle Park, NC, burned four heavy fuel oils and seven coals in three small combustion systems and measured size distributions and composition of the particles formed in the combustion process. The research found that, for heavy fuel oils, particle composition and size are dependent upon the combustion environment in the combustor. In the coolest test unit, unburned carbon in the fly ash was very high (70-90% by mass), and PM mass emissions were also high, with the majority of the mass being in the coarse (>2.5 µm in aerodynamic diameter) size range. In the hottest test unit, the PM mass emissions were approximately 50% of those from the coolest unit, unburned carbon levels were approximately zero, and the entire PM mass was in particles smaller than 1 μm in aerodynamic diameter. For coal, the NRMRL research identified a previously unreported trimodal particle size distribution, with an ultrafine (~ 0.1 μm in aerodynamic diameter) mode, a coarse (>5 μm in aerodynamic diameter) mode, and a central mode of particles between 2 and 4 μm in aerodynamic diameter. The central mode has a composition similar to the coarse mode, but significantly different from the ultrafine mode. It is hypothesized that the composition of the ultrafine coal particle fraction is similar to the fine particle fraction in heavy fuel oil, which has been shown to generate increased toxicological responses following pulmonary exposure in laboratory animals. These findings may have implications for future PM control strategies, given the influence of operating conditions and the water-soluble composition of the smallest particle fractions of PM from metal-bearing fossil fuels.

17. KEY WORDS AND DOCUMENT ANALYSIS					
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group			
Pollution	Pollution Control	13B			
Combustion	Stationary Sources	12B			
Mortality	·	05K			
Morbidity		06E			
Fuel Oil		11H, 21D			
Coal		08G			
Particle Size Distribution		14G			
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